10/533579

JC14 Rec'd PCT/PTO 02 MAY 2005

EXPRESS MAIL NO. EV336518308US

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant(s): Matthew Allen ANGLIN, et al.	) Re: Priority Claim
U.S. Appln. No.: not yet assigned	) Group: not yet assigned
U.S. Filing Date: concurrently herewith	) Examiner: not yet assigned
International Application No: PCT/AU2003/001443	)
International Filing Date: 31 October 2003	) Our Ref.: B-5691PCT 622624-8
For: "FIRE RESISTANT MATERIAL"	) Date: May 2, 2005

35 U.S.C. 119 CLAIM TO PRIORITY

MAIL STOP PCT
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Attn: United States Designated/Elected Office (DO/EO/US)

Sir:

Prior PCT International Application No. PCT/AU2003/001443, designating the U.S., claims foreign priority as follows:

COUNTRY	FILING DATE	SERIAL NUMBER
Australia	31 October 2002	2002952373

The certified copy has been filed in prior PCT International Patent Application No. PCT/AU2003/001443.

Applicants hereby confirm that this claim for priority applies to the above-identified U.S. International stage application.

Respectfully submitted,

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AUSTRALIA

Patent Office
Canberra

I, JANENE PEISKER, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2002952373 for a patent by COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION and THE BOEING COMPANY as filed on 31 October 2002.

WITNESS my hand this
Thirteenth day of November 2003

JANENE PEISKER
TEAM LEADER EXAMINATION
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AUSTRALIA

Patents Act 1990

PROVISIONAL SPECIFICATION

Applicant(s):

COMMONWEALTH SCIENTIFIC AND INDUSTRIAL RESEARCH ORGANISATION

THE BOEING COMPANY

Invention Title:

FIRE RESISTANT MATERIAL

The invention is described in the following statement:

FIRE RESISTANT MATERIAL

The present invention relates to inorganic-organic hybrids (IOHs), methods for their preparation and their use as fire resistant materials or components of fire resistant materials. More specifically, the invention relates to polyamide fire resistant formulations containing IOHs which have application in the production of fire resistant articles or parts thereof for use in the transportation, building, construction and electrical or optical industries.

BACKGROUND OF THE INVENTION

Materials based on organic polymeric systems (plastics) are widely used in the transportation, building and construction industries. A drawback of many types of organic polymers is flammability which limits their suitability in applications requiring flammability resistance and where regulatory authorities govern flammability standards.

In commercially produced polymeric systems, flame-retarding species may be added during processing or forming of the materials to reduce the end products flammability. Conventional flame-retardants may be divided into different categories including:

Halogen based: which consist of either brominated or chlorinated chemicals such as brominated polystyrene or phenylene oxide (Dead Sea Bromine or Great Lakes CC) or bis(hexachlorocyclopentadieno) cyclooctane (Occidental CC).

Phorphorus based: which consist of a range of different chemistries from elemental phosphorus (Clarient), phosphonates (A&W antiblaze 1045), phosphonate esters (Akzo Nobel), phosphites, phosphates and polyphosphates including melamine phosphite and phosphate, ammonium and melamine polyphosphate (DSM Melapur).

Nitrogen based: such as melamine and its salts (US 4511 684 Schmidt & Hoppe).

Intumescent agents: incorporating (i) an acid source (carbonization catalyst) such as ammonium polyphosphate; (ii) a carbonization reagent e.g. polyhydric alcohols such as pentaerythritol; and (iii) a blowing reagent like melamine. Expandable graphite is also known to undergo thermal expansion on addition of heat.

Inorganic additives: such as magnesium hydroxide and aluminum hydroxide (Martinswerk), zinc borate (Fire Brake ZB, US Borax) and antimony trioxide.

Although the addition of fire retardants to polymeric systems may improve their fire performance other important properties are often adversely effected for example:

- Mechanical performance
- Surface finish
- Durability
- Smoke generation
- Toxicity
- Cost
- Recyclability

Furthermore, there has been considerable recent impetus to reduce the use of some flame-retardant classes due to toxicological or environmental concerns. Such legislation has placed pressure on the use of halogenated compounds and certain metal oxide synergists. Phosphorus-based flame-retardants such as phosphonates and elemental (red) phosphorus are also undesirable due to their regulation under chemical weapon acts and considerable manufacturing danger.

As far back as 1965, Jonas (GB 1114,174) teaches that the incorporation of organically modified clay into plastics reduces melt dripping during combustion.

More recently it has been shown that under certain synthetic or processing conditions, organically

modified clay may be nano-dispersed into polymeric materials to improve mechanical and fire performance.

Okada et al, (US 4739 007 (1988) Toyota) teaches that nylon 6 materials with improved mechanical and heat distortion temperature can be prepared by adding suitably modified clay during the synthesis of nylon 6. In this case the growing nylon chains force apart the clay platelets to form intercalated or exfoliated nanomaterial structures (so called in 'situ polymerisation' method).

A more commercially desirable method of nano-dispersing modified clay is described by Maxfield, et al, (WO 93/04118 WO 93/04117 (1993) Allied Signal). Maxfield teaches that clay-plastic nanomaterials with improved mechanical and heat distortion performance may be prepared by subjecting functionalised clay and molten plastics such as nylon6, nylon66 and PBT to shear forces.

Others have investigated the fire performance of plastics incorporating clay nano particles. Gilman has studied the fire performance of nylon-nanomaterials prepared through the 'in situ' polymerisation pathway using cone calorimetry (Proc. 43. Int. SAMPE Sympos., (1998), p1053-1066, Fire and Materials, 24, (2000), p201-208, Applied Clay Science, 15, (1999), p31-49). Improved heat release rates were achieved with the addition of commercially modified clay, without increasing toxic gas or smoke generation. Gilman teaches that the improved fire performance results from the nanoparticles both mechanically stabilizing the char and enhancing its barrier properties. Although Gilman's cone calorimetry tests suggest improved performance in terms of a reduction in heat release rate, no mention was made of other aspects of the materials fire performance in common tests described by bodies such as ASTM and FAA which are used to assess, regulate and qualify the fire worthiness of materials.

Other groups have reported that traditional flame-retardants and nano-dispersed clays can act synergistically to improve fire performance.

Klatt (WO 9836 022, (1998) BASF) teaches that nylon materials incorporating organically modified clay and red phosphorus synergistically improve fire performance to produce a VO rating in UL94 type vertical burn tests. However, such compositions are undesirable due to the danger associated with handling of elemental phosphorus.

Morton (WO 99/43747, (1999) General Electric Company) teaches that in certain polyester blends, phosphorus based flame retardants especially resorcinol diphosphate and organically modified clay act synergistically to improve fire performance. No mention, however, is made of other important aspect such as the effect on mechanical performance, smoke and toxic gas emission.

Takekoshim (US 5773 502 (1998) General Electric Company) teaches that conventional halogenated-Sb_2O_3 flame-retardant systems and organically modified clay can act synergistically. Takekoshim claims that nano-dispersed clay allows for reductions in the amount of Sb_2O_3 and halogenated flame retardant required to maintain a VO rating in the UL 94 flammability test. Clearly any use of halogenated flame retardant is undesirable.

Masaru, T (JP 10182141 (1998) Sumitoma, Chem Co.) disclose a fire resistant and thermally expandable material at temperatures between 100 to 150°C whereby blowing reagents such as those containing azo, diazo, azide or triazine compound are located between the layers of the silicate. In many polymeric systems, however, this flame retarding system is undesirable since they require moulding or forming at temperatures between 100°C to 150°C.

Inoue and Hosokawa (JP 10081510 (1998) Showa Denko K.K.) investigated the use of fluorinated synthetic mica exchanged with melamine (0.1 - 40%) and melamine

salts (<10%) as a means of flame proofing plastics in a two step extrusion process. They claim that a VO rated Nylon6 (UL94 vertical burn test) was achieved at a loading of 5 percent-modified mica when greater than 80% exfoliation occurred. The use of synthetic clays and multiple step processing is clearly undesirable from a commercial viewpoint. Inoue and Hosokawa do not disclose highly desirable chemistries and methodologies associated with triazine based formulations which effect mechanical and fire performance. Furthermore, they do not disclose important methodologies to flame retarded thin parts known by those in the art to be extremely difficult to render flame resistant whilst simultaneously reducing toxic gas and smoke generation during combustion.

In a later disclosure Inoue, H., and co-workers (US 6294599 (2001) Showa Denko K.K.) also teach that polyamides reinforced with fibrous additives may be rendered flame resistant through the addition of triazine-modified clay and additional flame retardant. They describe a highly rigid flame-retardant polyamide comprising a polyamide, silicate - triazine compound reinforcement and flame retardant/adjunct. The poor rheological properties of highly rigid polyamide formulations limit the inventions usefulness in preparing components made by conventional processing techniques such as rotational or blow moulding, that are complex or thin walled or which require high ductility or impact performance.

Brown, S.C. et al (WO 00/66657, Alcan International) disclose a polymeric material incorporating Cloisite montmorillonite in combination with $Al(OH)_3$ for the production of fire resistant cables. This strategy is clearly only suitable for plastics that are processed at low temperatures considering that $Al(OH)_3$ decomposes to release water vapor at temperatures above approximately 190°C.

Accordingly, there is a need for the development of new flame retarding systems which both meet the performance criteria associated with specific applications and address the above concerns.

SUMMARY OF THE INVENTION

According to one aspect of the present invention there is provided an inorganic-organic hybrid (IOH) which comprises:

(i) an expandable or swellable layered inorganic component; and

(ii) an organic component including at least one ionic organic component and optionally one or more neutral organic components, the one or more neutral organic components being intercalated between and/or associated with the layer(s) of the inorganic component.

Preferably, the organic component of the IOH includes one or more neutral organic components.

According to another aspect of the present invention there is provided a method for the preparation of the IOH defined above which comprises mixing components (i) and (ii) defined above in one or more steps.

The present invention also provides the use of the IOH defined above as a fire resistant material.

According to a further aspect of the present invention there is provided a fire resistant formulation which comprises:

(i) the IOH defined above; and

(ii) one or more flame retardants.

According to a still further aspect of the present invention there is provided a method for the preparation of the fire resistant formulation defined above which comprises mixing components (i) and (ii) as defined above in one or more steps.

The present invention also provides a polyamide fire resistant formulation which comprises either:

(A) (i) the IOH defined above; and

(ii) a polyamide based matrix; or

(B) (i) the fire resistant formulation defined above; and

(ii) a polyamide based matrix.

The present invention further provides a method for the preparation of the polyamide fire resistant formulation defined above which comprises dispersing the IOH or the fire resistant formulation defined above or the components thereof into the polyamide based matrix in one or more steps.

The polyamide fire resistant formulations of the present invention may be used to produce fire resistant articles or parts thereof.

Thus, the present invention provides a fire resistant article or parts thereof which is composed wholly or partly of the polyamide fire resistant formulation defined above.

The present invention also provides a method of preparing the fire resistant article or parts thereof defined above which comprises moulding or forming the polyamide fire resistant formulation defined above.

DETAILED DESCRIPTION OF THE INVENTION

For the purposes of this specification it will be clearly understood that the word "comprising" means "including but not limited to", and that the word "comprises" has a corresponding meaning. It should also be noted that for the purposes of this specification the terms "swellable" and "expandable" relating to the layered inorganic component are interchangeable.

The inorganic component is a swellable/expandable layered inorganic based material, rendered positively (or negatively) charged due to isomorphic substitution of elements within the layers, such as, those based on a 1:1 layered silicate structure such as kaolin and serpentine and a 2:1 layered silicate structure such as phyllosilicates, talc and pyrophyllite.

Other useful layered minerals include layered double hydroxides of the general formula $Mg_6Al_{3.4}(OH)_{18.8}(CO_3)_{1.7}.H_2O$ including hydrotalcites and synthetically prepared layered materials including synthetic hectorite, montmorillonite, fluorinated synthetic mica and synthetic hydrotalcite.

The group consisting of naturally occurring or synthetic analogues of phyllosilicates is particularly preferred. This group includes smectite clays such as montmorillonite, nontronite, beidellite, volkonskoite, hectonite, laponite, saponite, sauconite, magadiite, kenyaite, and vermiculite. Other useful layered minerals include illite minerals such as ledikite and mixtures of illite minerals with said clay minerals.

Naturally occurring phyllosilicates such as montmorillonite, hectonite, and laponite are most preferred. Such phyllosilicates with platelet thicknesses less than about 5 nanometers and aspect ratios greater than about 10:1, more preferably greater than about 50:1 and most preferably greater than about 100:1 are particularly useful.

The preferred inorganic materials generally include interlayer or exchangable metal cations to balance the charge, such as, alkali metals or alkali earth metals, for example, Na^+, K^+, Mg^{2+} or Ca^{2+}, preferably Na^+. The cation exchange capacity of the inorganic material should preferably be less than about 400 milli-equivalents per 100 grams, most preferably about 50 to about 200 milli-equivalents per 100 grams.

The organic component includes one or more ionic species that may be exchanged with the exchangeable metal ions associated with the inorganic component and optionally one or more neutral organic species which are intercalated between and/or associated with the layer(s) of the inorganic component and/or one or more coupling reagents.

The term "associated with" is used herein in its broadest sense and refers to the neutral organic component

being attached to the layer(s) of the inorganic component, for example, by secondary bonding interactions, such as, Van der Waals interactions or hydrogen bonding.

Suitable examples of ionic species include those that contain onium ions such as ammonium (primary, secondary, tertiary and quaternary), phosphonium or sulfonium derivatives of aliphatic, aromatic or aryl-aliphatic amines, phosphines and sulfides.

Such compounds may be prepared by any method known to those skilled in the art. For example, salts prepared by acid-base type reactions with mineral or organic acids including hydrochloric, sulfuric, nitric, phosphoric, acetic and formic acids, by Lewis-acid - Lewis-base type reactions or by reaction with alkyl halides to form quaternary salts for example using Menschutkin type methodology.

Ionic or neutral compounds which are known to decompose or sublime endothermically, and/or which release volatiles with low combustibility on decomposition and/or induce charring of organic species during thermal decomposition or combustion are particularly preferred.

Suitable species include neutral or ionic derivatives of nitrogen based molecules, such as, triazine based species, for example, melamine, triphenyl melamine, melam (1,3,5-triazine-2,4,6-triamine-n-(4,6-diamino-1,3,5-triazine-yl)), melem ((-2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene)), melon (poly{8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl)imino}), bis and triaziridinyltriazine, trimethylsilyltriazine, melamine cyanurate, melamine phthalate, melamine phosphate, melamine phosphite, melamine phthalimide, dimelamine phosphate, phosphazines and/or low molecular weight polymers with triazine and phosphazine repeat units or salts or derivatives of the above molecules including onium ion derivatives or salts or derivatives of isocyanuric acid, such as, isocyanuric acid, cyanuric acid, triethyl cyanurate, melamine cyanurate,

trigylcidylcyanurate, triallyl isocyanurate, trichloroisocyanuric acid, 1,3,5-tris(2-hydroxyethyl)triazine-2,4,6-trione, hexamethylenentetramine. melam cyanurate, melem cyanurate and melon cyanurate.

Reagents known to induce charring of organic species include derivatives of phosphoric acid or boric acid, such as ammonia polyphosphate and melamine polyphosphate, melamine phosphate ammonium borate.

In another embodiment of the invention, the preferred ionic compounds may be optionally used in combination with other ionic compounds, for example, those known to improve compatibility and dispersion between the layered inorganic material and polymeric matrices such as those described in WO 93/04118 for the preparation of nanomaterials. Amphiphilic molecules that incorporate a hydrophilic ionic group along with hydrophobic alkyl or aromatic moieties are preferred.

One or more coupling reagents may also be associated with the inorganic component. Suitable coupling reagents include organically functionalised silanes, zirconates and titanates. Examples of silane coupling reagents include tri-alkoxy, acetoxy and halosilanes functionalised with amino, epoxy, isocyanate, hydroxyl, thiol, mercapto and/or methacryl reactive moieties or modified to incorporate functional groups based on triazine derivatives, long chain alkyl, aromatic or alkylaromatic moities. Examples of zirconate and titanate coupling reagents include Teaz and Titan1.

It is known in the art that metal cations or anions associated with layered inorganic materials may be exchanged with organic ions through ion exchange processes. In a typical process, the layered inorganic material is first swollen or expanded in a suitable solvent(s) prior to ion exchange and then collected from the swelling solvent following agglomeration using methods such as filtration, centrifugation, evaporation or

sublimation of the solvent. Ion exchange techniques with suitable molecules are known to be a useful method of increasing the compatibility between clay and organic polymeric binders, thus aiding dispersion of clay platelets into polymeric based matrices on a nanometer scale.

We have discovered that the ion exchange process may be optionally carried out in the presence of one or more types of organic ion to produce an inorganic-organic hybrid with a plurality of functions. Without wishing to limit the present invention, such functions may include the presence of ions which promote dispersion, compatibility and interactions with the plastic matrix and ions useful to improve other properties such as fire performance. Generally during ion exchange the organic ions are added in molar excess of the ion exchange capacity of the inorganic material, preferably less than about 10-fold excess, more preferably less than about a 5-fold excess is required.

It has also been unexpectedly discovered that the ion exchange processes may be carried out in the presence of functional dissolved or partially dissolved neutral species. Without being limited by theory, it is proposed that at least a portion of the neutral species are trapped in the intergallery region or otherwise associated with the layered inorganic material following ion exchange. Such a process provides a useful mechanism of dispersing neutral additives on a molecular level into plastics. Again without being limited by theory, during melt processing at least partial exfoliation of the inorganic-organic hybrid allows the neutral molecules to diffuse away and become homogeneously dispersed with the matrix on a molecular level. This has a major impact on the performance of the resultant material since it is well known that efficient dispersion of all components in a plastic formulation, preferably on a nano- or molecular

scale, is an important factor for achieving optimum performance.

In another aspect of the invention, the IOH may be treated prior, during or following ion exchange with one or more coupling reagents as described above. The coupling reagents are derivatized to improve, for example, the compatibility and interactions between the inorganic phase and polymeric matrix or to attach other desirable functionalities to the inorganic layered phase.

Suitable flame retardants which retard flame propagation, heat release and/or smoke generation which may be added singularly or optionally synergistically to the IOH include:

- Phosphorus derivatives such as molecules containing phosphate, polyphosphate, phosphites, phosphazine and phosphine functional groups, for example, melamine phosphate, dimelamine phosphate, melamine polyphosphate, ammonia phosphate, ammonia polyphosphate, pentaerythritol phosphate, melamine phosphite and triphenyl phosphine.
- Nitrogen containing derivatives such as melamine, melamine cyanurate, melamine phthalate, melamine phthalimide, melam, melem, melon, melam cyanurate, melem cyanurate, melon cyanurate, hexamethylene tetraamine, imidazole, adenine, guanine, cytosine and thymine.
- Molecules containing borate functional groups such as ammonia borate and zinc borate.
- Molecules containing two or more alcohol groups such as pentaerythritol, polyethylene alcohol and carbohydrates, for example, glucose, sucrose and starch.
- Molecules which endothermically release non-combustible decomposition gases, such as, metal hydroxides, for example, magnesium hydroxide and aluminum hydroxide.
- Expandable graphite

The polyamide based matrix may be included in the fire resistant formulation in pellet, granule, flake

or powdered form. Suitable polyamides comprise generic groups with repeat units based on amides, such as, nylon4, nylon6, nylon7, nylon 11 and nylon12, nylon46, nylon66, nylon 68, nylon610, nylon612 and aromatic polyamides, for example, poly'm'phenyleneisophthalamine and poly'p'phenylene'terephthalmamide.

It will be appreciated that the polyamide based matrix may include co-polymers, blends and alloys. The co-polymers may be made up of two or more different repeat units one of which is an amide. Such co-polymers may be prepared by any suitable methods known in the art, for example, at the point of initial polymerisation or later through grafting or chain extension type reactions during processing. The polyamide blends and alloys may be prepared using any method known to those skilled in the art including melt or solution blending. Blending or alloying the polyamide with other polymers may be desirable to improve properties such as toughness, modulus, strength, creep, durability, thermal resistance, conductivity or fire performance.

Nylon11 and nylon12 and their respective co-polymers, alloys and blends are particularly preferred.

The polyamide formulation can also optionally contain one or more additives known in the art of polymer processing, such as, polymeric stabilizers, for example, UV, light and thermal stabilizers; lubricants; antioxidants; pigments or other additives to alter the materials optical properties; conductive fillers or fibers; release agents; slip agents; plasticizers; and processing agents, for example, dispersing reagents, foaming or blowing agents, surfactants, waxes, coupling reagents and free radical generating reagents.

A particularly preferred formulation comprises a polyamide such as nylon11 and/or nylon12; an IOH consisting of montmorillonite modified as outlined above and additionally melamine cyanurate and/or melam (1,3,5-triazine-2,4,6-triamine-n-(4,6-diamino-1,3,5-triazine-yl))

cyanurate, and/or melem ((-2,5,8-triamino-1,3,4,6,7,9,9b-heptaazaphenalene)) cyanurate and/or melon (poly{8-amino-1,3,4,6,7,9,9b-heptaazaphenalene-2,5-diyl)imino}) cyanurate optionally with $Mg(OH)_2$ and minor polymeric additives.

The polyamide formulation preferably contains a polyamide based matrix in an amount of from about 50 to about 95% w/w, an IOH in an amount less than about 25% w/w and optionally a flame retardant and/or known polymer additives in an amount less than about 30% w/w, but in some cases preferably above about 10% w/w.

It has been discovered that the IOH may be readily dispersed into the polyamide based matrix during the compounding (mixing) stage. Without wishing to be limited by theory, it is proposed that ion exchange enhances the layered IOHs compatibility with polyamides compared with unmodified inorganic layered materials. This heightened compatibility in combination with sufficient mixing forces, appropriate mixing sequence, screw design and time allows the organically modified platelets associated with the IOH to be at least partially exfoliated into the polyamide and hence dispersed at least partially on a nanometer scale. This process also provides a useful mechanism of dispersing into the polyamide any neutral molecules associated with the IOH on a molecular level.

Dispersion of the various components of the fire resistant formulation including the IOH is aided by grinding prior to mixing. Grinding is achieved using any suitable grinding equipment including ball mills, ring mills and the like. It is preferable that the components including the IOH is ground to a particle size less than about 200 microns, more preferably less than about 50 microns, most preferably less than about 20 microns. The hybrid material may also be ground using specialty grinding equipment allowing grinding to nanometer sizes.

Dispersion may be affected using any suitable melt or solution based mixing process allowing sufficient shear rate, shear stress and residence time to disperse the IOH at least partially on a nanometer scale. Such processes may be conducted in a batch process using internal mixers, such as, Banbury and Brabender/Haake type mixers, kneaders, such as, BUS kneaders and continuous mixing processes including continuous compounders, high intensity single and twin screw extrusion.

Melt processing is preferred and in a particularly preferred embodiment, twin screw extruders with an L:D ratio of at least about 24, preferably more than about 30 equipped with at least one and preferably multiple mixing and venting zones are employed for dispersion. Such screw configurations useful for dispersive and distributive mixing are well known to those in the art. A particularly useful system has been found to be that illustrated in Figure 1.

The components of the formulation may be added in any order or at any point along the extruder barrel. Since polyamides are susceptible to hydrolysis it is preferable that the components are dried prior to processing and/or mechanisms to remove water vapor such as vents or vacuum ports available during processing. In a preferred embodiment, all of the components are added at one end of the extruder. In another preferred embodiment, a polymeric binder and optionally minor components are added at one end of the extruder and the IOH and optionally minor components at a later point/s. In still another preferred embodiment, the IOH portion of the polymeric binder and optionally minor components are added at one end of the extruder with the remaining portion of the polymeric binder and optionally minor components are added at a later point/s. Following extrusion the molten composition is cooled by means of water bath, air knife or atmospheric cooling and optionally cut into pellets.

Preferably all of the major and minor components of the system can be combined in as few a mixing steps as possible, most preferably in a single mixing step.

The moulding or forming of the polyamide formulation into fire resistant articles or parts thereof can be carried out using any method known to those in the art including processes such as extrusion, injection moulding, compression moulding, rotational moulding, blow moulding, sintering, thermoforming, calending or combinations thereof.

In one embodiment of the invention the fire resistant polyamide system containing the major and minor components is moulded or formed into parts having wall thickness less than about 25 mm, preferably less than about 5 mm, most preferably less than 1.5 mm. Such parts include but are not limited to tubes, complex moulded hollow parts, sheets and complex moulded sheets and other complex objects that are moulded or formed using techniques, such as, extrusion, injection moulding thermoforming and rotational moulding.

In the simplest process, the article or part is directly produced during compounding for example by locating a die at the end of the extruder allowing the shape of the extrudate to be modified as required. Examples of such components include simple parts such as film, tape, sheet, tube, rod or string shapes. The process may also involve multiple layers of different materials one of which being the said polymeric system built up by processes known to those in the art including co-extrusion.

In another preferred embodiment, the formulation is moulded or formed in a separate step using techniques such as injection, compression or blow moulding. Such parts are generally more complex in nature compared with parts formed by extrusion alone, their design only limited by the requirements of the moulding tool / process employed. Suitable examples include but are not limited to

stowage bin hinge covers, ECS duct spuds, latches, brackets, passenger surface units and the like.

It is noted that for certain applications it may be preferable that the fire resistant polyamide formulation is ground to a powder. In such cases it has unexpectedly been found that grinding of the said formulation using cryogenic or atmospheric grinding techniques known to those in the art may be carried out without significantly effecting the performance of the system. Such moulding applications include selective laser sintering, rotational moulding, and extrusion. Suitable examples including but not limited to environmental control systems (air-conditioning ducts) and the like.

In other preferred applications, the polymeric formulation may be first formed into a sheet or film, for example, through extrusion, blow moulding, compression moulding or calending. The sheet may be subsequently moulded to a desired shape using thermoforming techniques. In yet another application, the sheet or film may be used to prepare reinforced thermoplastic laminates with woven fabrics prepared from surface modified or natural glass, carbon or aramid using techniques such as compression moulding or resin infusion/transfer. Again, the laminate sheet hence formed may be further moulded to a desired shape using techniques such as thermoforming.

The present invention is useful for producing polyamide materials with favorable rheological properties for molding including thin or intricate articles or parts thereof which maintain mechanical properties close to or exceeding that of the virgin polyamide matrix and which show improved fire performance in standard tests through resisting combustion by self-extinguishing when ignited, limiting flame propagation, and generating low smoke and toxic gas emissions. Such articles or parts thereof are useful for applications which require superior fire performance and in industries that are regulated for fire

performance including transport, for example, air, automotive, aerospace and nautical; building and construction; and electrical or optical, for example, cables, wires and fibers.

EXAMPLES

The invention will now be described with reference to the following non-limiting examples.

In the examples, reference will be made to the accompanying drawings in which:

Figure 1 is a diagram showing the twin screw extruder - screw and barrel configuration;

Figure 2 is a graph showing the XRD results for Example 7;

Figure 3 is a graph showing the XRD results for Example 8;

Figure 4 is a graph showing the XRD results for Example 9;

Figure 5 is a graph showing the cone calorimeter heat release rate values for Example 15;

Figure 6 is a graph showing the FAA 12s vertical burn extinguishing times (0.75mm) for Example 15;

Figure 7 is a graph showing the tensile strengths for Example 15; and

Figure 8 is a graph showing the notched impact performance for Example 15.

General Conditions : Tables 1a & 1b and 2 Outline General Conditions/Procedures Associated With The Examples

Table 1a: Processing Equipment and Conditions

Equipment	Type
Twin screw extruder	Berstorff ZE 25 mm modular co-rotating twin screw extruder coupled to a Haake Rheocord motor drive and torque cell L:D ratio = 36:1 Screw and barrel configuration presented in Figure 1, Screw speed 300 rpm Feed rate ~1.2 Kg/hour *Residence time average 2 min* Flat 200°C temperature profile from throat to die
Batch Mixer	Haake R3000 batch mixer connected to torque rheological load cell, pneumatic ram, roller rotors Rotor speed – 5 min 60 rpm, 10 min 120 rpm Temperature 190°C
Injection Moulding	Battenfeld 80 ton BA 800 CDC injection moulding machine Nylon12 samples: Temperature profile: Zone 1 2 3 Nozzle Die Temp (°C) 215 220 225 225 70°C **ASTM test samples:** Injection pressure gradient 800 to 600 bar, cavity pressure 400 bar Holding pressures 600 to 0 bar Cooling time 30sec **Cone Calorimetry Samples:** Injection pressure gradient 950 to 650 bar, cavity pressure 325 bar Holding pressures 650 to 0 bar Cooling tine 60 sec Polyetherimide (ULTEM 9075) samples were moulded by GE plastics Australia
Compression Moulding	Assett 2.5 MPa pneumatic press, 45 cm platens, heating (400°C) and cooling Moulding platen temperature 220°C

Table 2.1A: Commercially Available Reagents

Reagent	Trade name	Supplier
Montmorillonite – organic modified	Cloisite 93A	Southern Clay Products
Montmorillonite – organic modified	Cloisite 30B	Southern Clay Products
Montmorillonite	Cloisite Na^+	Southern Clay Products
Nylon12	Vestamid	Degussa
Nylon12	Grilamid	EMS
Cyanuric acid	Cyanuric acid	Aldrich
Melamine cyanurate	Fyrol MC	Akzo-Nobel
Melamine phosphate	Fyrol MP	Akzo-Nobel
Melamine polyphosphate	Melapur 200	DSM Melapur
Melamine	Melamine	Aldrich
Pentaerythritol	Pentaerythritol	Aldrich
Magnesium hydroxide	Magnifin	Martinswerk
Ammonia polyphosphate	Antiblaze MC	Rhodia
Pentaerythritol phosphate	NH-1197	Great Lakes
Pentaerythritol phosphate Blend	NH-1511	Great Lakes
Zinc borate	Fire Brake ZB	US Borax

Table 2: Characterization Techniques, Conditions and Sample Preparations

Equipment	Type
X-ray diffraction (XRD)	Phillips PW 1729, $CuK_{\alpha 1}$ source $\lambda = 0.154$ nm Powders were ground to a particle size of less than 100 micron Plastics were compression moulded (210°C) to a thickness of 100 micron
Transmission Electron Microscopy (TEM)	Hitachi H-7500 operating at an electron potential of 120 kV 100 nm thick sections were prepared by ultra microtomy
DSC	Cryogenic TA 2920 MDSC employing Advantage software, 10°C and 20°C/min ramp rate rates for heating and cooling for general thermal and glass transition respectively Calibrated against, Indium, distilled water, cyclohexane and sapphire Powders were ground to a particle size of less than 100 micron Plastics were compression moulded (210°C) to a thickness of 100 micron with quench cooling, 5mm diameter specimens were punched from the moulded sheet
TGA/DTA	Thermal Sciences, PL-STA, referenced against Al_2O_3 Heating rate ramp10°C / min Powders were ground to a particle size of less than 100 micron Plastics were compression moulded (210°C) to a thickness of 100 micron with quench cooling, 4mm diameter specimens were punched from the moulded sheet
Equipment	**Type**
Cone Testing	ASTM E 1354 - 92 Modified from the original Stanton-Redcroft model, CSIRO developed software Radiant flux 35 kW/m^2 3 repeats per sample, ASTM E1356 Following injection moulding, samples (100x100x6mm) were conditions for 7 days at 23°C at 50% RH.
Radiant Panel	Conducted as per FAA specification (DOT FAA/AR-0012) And as Outlined in ASTM E648 – 93a

Specific Optical Density of smoke Generated By Solid Materials and gas emission	ASTM E662 – 93 for optical density with gas released by samples during the test analyzed for HF, HCl, HCN, H_2S, NO_x, HBr, PO_4, SO_2
Vertical Burn	Vertical burn tests according to UL94 or FAA specifications. **UL94 specification –** One 10 sec application of flame from a 10 mm burner to 125x12.3x3.2 mm samples according to UL specifications 2000. Flame extinguish times were monitored over at least 3 samples Extinguishing times, VO <10s, V1 <30s, V2 <30s Cotton Wool Ignition No No Yes **FAA (DOT FAA/AR-0012) and ASTM F501-93** One 12s application of flame from a 10 mm burner to 300x75x1.6 mm samples according to FAA specification 2000 Pass FAA test requirement: Flame extinguished <15sec Drip extinguished <5 sec Burn height <203 mm
Notched Impact Testing	Radmana ITR 2000 instrumented impact tester Izod mode Impact strain rate 3.5 ± 0.2 m/sec 10 repeats per sample, ASTM 256 Following injection moulding, samples were stored for 24 h in desiccated containers, notched according to the ASTM 256 standard and tested 'dry as moulded'
Tensile Testing	Instron tensile testing apparatus (5565) utilizing a 30 kN load cell 50 mm/min strain rate 5 repeats per sample, ASTM 638 External extensometer used for independent modulus measurements ASTM D5938 Following injection moulding, samples were stored for 24 h in desiccated containers and tested 'dry as moulded'

Methods for Preparing Inorganic-Organic hybrids & Melamine Cyanurate, Examples 1-6

Example 1: Preparation of melamine hydrochloride modified montmorillonite

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 80°C distilled water (2% w/w) and mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g cloisite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 75°C prior to processing or analysis.

XRD ($CuK_{\alpha 1}$ source λ = 0.154 nm)

Cation	Na^+	Melamine.HCl modified Montmorillonite
XRD d_{001}	1.10 nm	1.27 nm

Results indicate that with ion exchange montmorillonite's intergallery spacing is increased from 1.10 nm to 1.27 nm. This result is consistent with sodium ions being replaced by protonated melamine ions in the intergallery region during ion exchange.

Example 2: Preparation of melamine hydrochloride modified montmorillonite in the presence of melamine

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 80°C distilled water (2% w/w), melamine added (1.4 mmol/100 g cloisite) and the

solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g cloisite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 75°C prior to processing or analysis.

XRD ($CuK_{\alpha 1}$ source λ = 0.154 nm)

Cation	Na^+	Melamine and Melamine.HCl modified Montmorillonite
XRD d_{001}	1.10 nm	1.39 nm

Results indicate that montmorillonite modified by melamine hydrochloride in the presence of melamine has an expanded intergallery spacing compared with both montmorillonite that is modified with melamine hydrochloride or sodium ions. This result is consistent association/entrapment of the neutral melamine with the clay during ion exchange.

<u>Example 3:</u> <u>Preparation of melamine cyanurate hydrochloride modified montmorillonite</u>

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 90°C distilled water (2% w/w), cyanuric acid added (1.4 mmol/100 g cloisite) and the solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g cloisite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The

resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 75°C prior to processing or analysis.

XRD ($CuK_{\alpha 1}$ source λ = 0.154 nm)

Cation	Na^+	Melamine cyanurate.HCl modified montmorillonite
XRD d_{001}	1.10 nm	1.42 nm

Results from Example 3 indicate that the intergallery spacing of montmorillonite is expanded further when exchanged with melamine cyanurate ion compared with sodium ion or melamine ion modified montmorillonite (Example 1) due to its larger size and hence steric impact.

<u>Example 4:</u> <u>Preparation of melamine and melamine cyanurate modified clay in presence of melamine and melamine cyanurate</u>

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 90°C distilled water (2% w/w), cyanuric acid added (1.4 mmol/100 g cloisite) and the solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g cloisite) and melamine (1.4 mmol/100g cloisite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 75°C prior to processing or analysis.

XRD ($CuK_{\alpha 1}$ source λ = 0.154 nm)

Cation	Na^+	Melamine and Melamine cyanurate.HCl modified montmorillonite
XRD d_{001}	1.10 nm	1.53 nm

The results from Example 4 indicate that the intergallery spacing of montmorillonite exchanged with melamine cyanurate ion in the presence of melamine is larger than both sodium ion or melamine cyanurate ion exchanged montmorillonite (Example 3). This result is consistent with association/entrapment of the neutral melamine with the clay during ion exchange.

Example 5: Preparation of melamine and trimethyl cetylammonium and melamine hydrochloride modified clay

Montmorillonite exchanged Na^+ (Cation Exchange Capacity (CEC) = 92 meq/100g) was suspended in 90°C distilled water (2% w/w), and the solution mechanically stirred at 1500 rpm for 60 min. Melamine monohydrochloride salt (1.4 mmol/100g cloisite) and tirimethylcetylammoniun chloride (1.4 mmol/100g cloisite) was then added to the solution and the resultant suspension allowed to cool with continued stirring for a further 150 min. Following filtration of the suspension, the precipitate was thoroughly washed with warm distilled water and then preliminary dried under vacuum (75°C). The resultant granular organically modified clay was ground to a particle size of less than 45 micron and then further dried at 75°C prior to processing or analysis.

XRD ($CuK_{\alpha 1}$ source λ = 0.154 nm)

Cation	XRD d_{001}
Na^+	1.10 nm
Trimethylcetylammonium chloride	1.84 nm
Melamine and Trimethylcetylammonium chloride modified montmorillonite	1.68 nm

The results from Example 5 indicate that the intergallery spacing of montmorillonite exchanged with both trimethylcetylammonium chloride and melamine hydrochloride is larger than sodium but smaller than trimethylcetylammonium ion exchanged montmorillonite. This result is consistent with trimethylcetylammonium chloride and melamine hydrochloride being present in the intergallery spacing of the modified montmorillonite.

<u>Example 6:</u> <u>Preferred Preparation of Melamine Cyanurate</u>

In separate flasks, cyanuric acid (129 g 1.0mol) and melamine (130g, 1.03 mol) were dissolved in boiling distilled water (3.0 L). With rapid stirring (1200 rpm), the melamine solution was added to the cyanuric acid solution and the resultant mixture allowed to cool to 50°C over two hours with continued stirring. The melamine cyanurate precipitate was filtered, thoroughly washed with warm distilled water and dried to constant weight prior to grinding to a particle size less than 45 micron for future compounding or analysis.

FTIR analysis of the synthesized melamine cyanurate confirmed the successful synthesis of the compound as indicated by the following characteristic absorptions peaks (KBr) ν_{max} 3391, 3230, 2800-2100 broad, 1780, 1736, 1662, 1535, 1448 cm^{-1}.

Melt Dispersion of Components and Formulation of Fire resistant Materials Example 7-14

While each of the following examples use Nylon12 as the polyamide based matrix, the person skilled in the art will appreciate that since nylons in general such as Nylon6, Nylon66 and Nylon12 are known to decompose and combust by a similar mechanism, the examples for fire retarding Nylon12 are also applicable to other nylons.

<u>Example 7:</u> <u>Processing (table 2), XRD (figure 2), mechanical (table 3) and fire performance (tables 4 & 5) of nylon12 modified with commercially available clay during melt processing.</u>

The following example indicates that the processing rheology of Nylon 12 is not effected by the melt dispersion of commercially available 'organoclay' at least partially on a nanometer scale (XRD). This dispersion results in improved mechanical performance and fire performance as illustrated by cone calorimetry but poor performance compared with conventional flame retarded nylon 12(FR Nylon12) in terms of vertical burn results

<u>Table 2: Torque Rheology</u>

Extrusion Torque Rheology					
Material	**Rotamoulding Grade Nylon12 Composition (±3Nm)**				
% Cloisite 30B	0	0.75	1.5	5.0	7.0
Torque (Nm) (±3Nm)	105	100	95	91	87

Batch mixer torque rheology (120rpm) Extrusion Grade Nylon12				
Material	Nylon12	Nylon12 + 5% 30B organoclay	Nylon12 + 5% 93A organoclay	Nylon12 + 5% Na^{+} Clay
Torque (Nm)	47	44	47	49

Table 3: Mechanical Performance

	Nylon12	0.75% 30B Organoclay	1.5% 30B Organoclay	5.0% 30B Organoclay	7.2% 30B Organoclay	FR N12
Modulus (MPa)	1110	1187	1227	1470	1700	1712
Tensile Strength (MPa)	41.2	53	52.3	57	44.6	48
Impact (k/m^2)	4006	6200	8100	6700	3700	2200

Table 4: Fire Testing Cone Results

Material	Peak Heat Rel^d kW/m^2	Mass Loss Rate g/m^{2}s	CO Prod^n Kg/Kg	CO_2 Prod^n Kg/Kg	SEA (Smoke) m^2/Kg
FR Nylon 12	1800	18.6	0.01	1.2	100
Nylon12	1344	17.1	0.03	1.6	385
Nylon12, 0.75% 30B Organoclay	740	13.3	0.01	1.0	360
Nylon12, 1.5% 30B Organoclay	620	12.8	0.02	1.5	382
Nylon12, 5.0% 30B Organoclay	536	10.8	0.02	1.5	382
Nylon12, 7.1% 30B Organoclay	447	10.0	0.02	1.5	410

Table 5: Vertical Burn Results

Material	UL94 (3.2 mm)	FAA (1.6 mm)
FR Nylon 12	VO	Fail
Nylon12	HB	Fail
Nylon12, 0.75% 30B Organoclay	V2	Fail
Nylon12, 1.5% 30B Organoclay	V2	Fail
Nylon12, 5.0% 30B Organoclay	V1	Fail
Nylon12, 7.1% 30B Organoclay	V1	Fail

Example 8: Processing (table 6), XRD (figure 3), mechanical (table 7) and fire performance (table 8-11) of nylon12 modified with commercially available clay and flame retarding additives (melamine cyanurate) during melt processing

The following example indicates that the processing rheology of Nylon 12 is not effected by the melt dispersion of commercially available 'organoclay' and flame retardant at least partially on a nanometer scale (XRD). This dispersion results in improved mechanical and excellent cone calorimetry and vertical burn results (>1.6 mm) compared with conventionally flame retarded nylon12. Although samples of 0.75 mm provide good smoke and toxic gas release results they fail FAA type 12 sec vertical burn testing and perform badly in radiant panel tests.

Table 6: Processing Rheology

Material	Torque (Nm)
Nylon 12	105
Nylon 12, 3% Cloisite 30B, 15% Melamine Cyanurate	102
Nylon 12, 1.5% Cloisite 30B, 15% Melamine Cyanurate	104
Nylon 12, 0.75% Cloisite 30B, 15% Melamine Cyanurate	107

Table 7: Mechanical Performance

Formulation	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m^2)
N12, 3% 30B organoclay, 10% Melamine Cyanurate	1505	38.5	54	3100
N12, 1.5% 30B organoclay, 10% Melamine Cyanurate	1471	38.1	222	4100
N12, 0.75% 30B organoclay, 10% Melamine Cyanurate	1380	38.1	291	4600
Nylon12	1110	41.2	640	4600
FR-Nylon12	1712	48.1	77	2100

Standard Deviation -Modulus<4%, Strength<3%, Elongation<10%, Impact <11%

Table 8: Fire Testing Cone Calorimetry

Material	Peak Heat Rel^{d} kW/m^2	Mass Loss Rate g/m^2s	CO Prod^{n} Kg/Kg	CO_2 Prod^{n} Kg/Kg	SEA (Smoke) m^2/Kg
FR Nylon 12	1800	18.6	0.01	1.2	100
R-Nylon12	1344	17.1	0.03	1.6	385
Nylon12, 3% 30B organoclay, 10% Melamine Cyanurate	670	13.9	0.01	1.6	220
Nylon12, 1.5% 30B organoclay, 10% Melamine Cyanurate	695	14.1	0.01	1.6	240
Nylon12, 0.75% 30B organoclay, 10% Melamine Cyanurate	782	16.1	0.01	1.7	280

Table 9: Vertical Burn Results

Material	UL94 (3.2 mm)	FAA (1.6 mm)	FAA (0.75 mm)
FR Nylon 12	V0	Fail	Fail
R-Nylon12	HB	Fail	Fail
Nylon12, 3% 30B organoclay, 10% Melamine Cyanurate	V0	Pass	Fail
Nylon12, 1.5% 30B organoclay, 10% Melamine Cyanurate	V0	Pass	Fail
Nylon12, 0.75% 30B organoclay, 10% Melamine Cyanurate	V0	Pass	Fail

Table 10: Vertical Burn, Radiant Panel and Smoke Test Results (0.75mm)

Sample Nylon 12 +	Flammability 0.75mm	Smoke Ds	Radiant Panel
Nylon12, 0.75% 30B organoclay, 10% Melamine Cyanurate	Fail	4.88	Full length burn
Nylon12, 1.5% 30B organoclay, 10% Melamine Cyanurate	Fail	11.86	Full length burn
Nylon12, 3% 30B organoclay, 10% Melamine Cyanurate	Fail	21.45	Full length burn

Table 11: Toxic Gas Emission

Toxic Gas	Nylon 12 +		
PPM	Nylon12, 0.75% 30B organoclay, 10% Melamine Cyanurate	Nylon12, 1.5% 30B organoclay, 10% Melamine Cyanurate	Nylon12, 3% 30B organoclay, 10% Melamine Cyanurate
HF	3	3	5
HCl	1	1	3
HCN	4	4	4
H_2S	-	-	-
NO_x	2	2	1
HBr	1	1	1
PO_4	-	-	-
SO_2	1	1	1

Example 9: Processing (Table 12), XRD (Figure 4), mechanical (Table 13) and fire performance (Table 14-16) of nylon12 modified with IOHS incorporating montmorillonite modified with melamine hydrochloride/melamine and flame retarding additives (melamine cyanurate) during melt processing

The following example indicates that the processing rheology of Nylon 12 is not effected by the melt dispersion modified clay and flame retardant at least partially on a nanometer scale (XRD). Such dispersion results in improved mechanical and vertical burn results compared with conventionally flame retarded nylon12. Samples of 0.75 mm provide good smoke and toxic gas release results and pass FAA type 12s vertical burn tests and perform better in radiant panel tests

Table 12: Processing Rheology

Rotamoulding Grade Material	Torque
Nylon 12	105
Nylon 12, 3% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	105
Nylon 12, 1.5% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	106
Nylon 12, 0.75% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	103

Table 13: Mechanical Performance

% Cloisite 30B	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m^2)
Nylon12	1110	41.2	640	4600
FR-Nylon12	1712	48.1	77	2100
R-Nylon12, 3% melamine.HCl/ melamine montmorillonite 10% Melamine Cyanurate	1443	39.7	140	3900
R-Nylon12, 1.5% melamine.HCl/ melamine montmorillonite 10% Melamine Cyanurate	1398	39.0	215	4200
R-Nylon12, 0.75% melamine.HCl/ melamine montmorillonite 10% Melamine Cyanurate	1349	38.9	375	4700

Standard Deviation -Modulus<3%, Strength<3%, Elongation<8%, Impact <9%

Table 14 Fire Performance - Vertical Burn

Material	UL94 (3.2 mm)	12s Vertical Burn (1.6 mm)	12s Vertical Burn (0.75 mm)
FR Nylon 12	VO	Pass	Fail
R-Nylon12	HB	Fail	Fail
R-Nylon12, 3% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	V0	Pass	Pass
R-Nylon12, 1.5% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	V0	Pass	Pass
R-Nylon12, 0.75% melamine.HCl/melamine montmorillonite, 10% Melamine Cyanurate	V0	Pass	Pass

Table 15 Fire Performance

Sample Nylon 12 +	12s Vertical Burn 0.75mm	Smoke Ds	Radiant Panel
0.75% melamine.HCl/melamine montmorillonite. / melamine cyanurate	2.4 sec 0.2 inch no drips	6.79	5 sec/ 1.0 inches
1.5% melamine.HCl/melamine montmorillonite. / melamine cyanurate	2.7 sec 2.7 inches no drip	9.83	3 sec 1.0 inches
3.0% melamine.HCl/melamine montmorillonite. / melamine cyanurate	2.1 sec 2.7 inches no drip	3.31	2 sec 1.0 inches

Table 16 Toxic Gas Emission

Toxic Gas	Nylon 12 +		
PPM	0.75% melamine.HCl/melamine montmorillonite /melamine cyanurate	1.5% melamine.HCl/melamine montmorillonite / melamine cyanurate	3.0% melamine.HCl/melamine montmorillonite. / melamine cyanurate
HF	6	4	3
HCl	1	1	1
HCN	8	7	7
H_2S	-	-	-
NO_x	3	2	2
HBr	1	1	1
PO_4	-	-	-
SO_2	1	1	1

Example 10: The following example illustrates the effect of processing parameters on performance of a nylon12 formulation incorporating an inorganic-organic hybrid based on melamine hydrochloride/melamine modified montmorillonite + flame retardant (melamine cyanurate)

Results indicate the robustness of the formulation to different processing conditions.

Table 17 Mechanical Performance

Conditions	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m^2)
180 temp	1300	37.6	130	5100
190 temp	1420	37.9	210	5300
200 temp	1420	38.4	250	4800
210 temp	1520	38.8	210	4600
Screw Speed 150	1500	37.7	200	5300
Screw Speed 400	1530	39.6	160	4100

Standard Deviation -Modulus<3%, Strength<3%, Elongation<8%, Impact <9%

Table 18 Fire performance

Conditions	0.75mm 12 sec Vertical Burn	Flame out Time (sec)
180 temp	Pass	5
190 temp	Pass	4
200 temp	Pass	5
210 temp	Pass	6
Screw Speed 150	Pass	2
Screw Speed 400	Pass	7

Example 11: The following example illustrates the effect of different flame retardants on the performance of nylon12 with an inorganic-organic hybrid (IOH) incorporating melamine hydrochloride/melamine modified montmorillonite + various flame retardants

The results presented in table 19 and 20 demonstrate that materials incorporating the IOH and melamine cyanurate provide both excellent mechanical and fire performance. Sample containing melamine phthalate and pentaerythritol phosphate also provide excellent fire performance with lower mechanical performance results. Samples containing IOHMS with melamine cyanurate and $Mg(OH)_2$ provide the best mechanical performance in terms of impact, modulus, and strength also excellent vertical burn performance.

Table 19 Mechanical Performance

Flame Retardant (1.5% melamine hydrochloride/ melamine modified montmorillonite + 15%.)	Tensile Modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)	Notched Impact Strength (J/m^2)
Melamine cyanurate	1460	39	250	4800
Melamine phosphate	1540	41.9	26	2500
Melamine polyphosphate	1500	40.4	35	3000
Melamine phthalate	-	-	-	-
Ammonia polyphosphate	1410	41.0	270	4100
Pentaerythritol phosphate	1420	43.5	24	1500
Pentaerythritol phosphate	1160	43.6	43	800
Melamine cyanurate / $Mg(OH)_2$	1628	43.6	-	4800

Table 20 Fire Performance

Flame Retardant (1.5% melamine hydrochloride modified montmorillonite + 15%)	UL 94 Test (3.2 mm)	Flame out time sec	12 sec FAA burn test (0.75 mm)	Flame out time (sec)
Melamine cyanurate	V0	<7	Pass	<3
Melamine phosphate	V2	<30	Fail	>15
Melamine polyphosphate	V2	<20	Fail	>15
Melamine phthalate	V0		Pass	<10
Ammonia polyphosphate	V2	<20	Fail	>15
Pentaerythritol phosphate	V2	<20	Fail	>15
Pentaerythritol phosphate	V0	<15	Pass	<12
10% Melamine cyanurate / 5% $Mg(OH)_2$	V0	<15	Pass	<10

Example 13: The following example illustrates the effect of different grades of melamine cyanurate on the fire performance of the fire resistant system

The results indicate that the synthesis conditions and mole ratio of reactants used to prepare melamine cyanurate play an important part in governing the fire performance of the material system. Synthesis conditions and mole ratio of reactants effect the fire performance of the resulting material as illustrated in Table 21 which compares the performance of materials prepared with melamine cyanurate synthesized in Example 6 with that purchased from AKZO-Nobel.

Table 21 Mechanical & Fire Performance

Specimen (N12 + 1.5% melamine modified clay +)	Extruder Torque Nm	Ultimate Tensile Strength MPa	Tensile Modulus MPa	Notched Impact Strength J/m^2	0.75 mm FAA 12 sec Vertical Burn**
10% melamine cyanurate (synthesized)	100	41	1440	4700	Pass (<3 sec, 0.5 inch)
15% melamine cyanurate (synthesized)	100	39.3	1420	4700	Pass (<2 sec, 0.5 inch)
10% melamine cyanurate (Akzo Nobel)	100	41.7	1490	5000	Fail (<24 sec, 3.5 inch)
15% melamine cyanurate (Akzo Nobel))	100	39.5	1531	4100	Pass (<5 sec, 0.5 inch)

**(average flame out time sec / burn length average)

Example 14: The following example illustrates the performance of Nylon12 prepared with the inorganic-organic hybrid prepared in Examples 1-4 and commercially produces melamine cyanurate (AKZO-Nobel)

The results indicate superior fire performance of samples containing the intercalated and modified IOH compared with that prepared with just melamine hydrochloride modified montmorillonite.

Table 22 Mechanical and Vertical Burn Performance

Specimen * (Nylon 12 +...)	Ultimate Tensile Strength (MPa)	Tensile Modulus (MPa)	Notch ed Impact Strength J/m^2	0.75 mm FAA 12 sec Vertical Burn (Flame out time sec, burn length))
1.5% melamine modified clay + 10% melamine cyanurate	41.7	1490	5000	Fail (<24 sec, <3.5 inch)
1.5% melamine modified clay + 15% melamine cyanurate	39.5	1531	4100	Pass (<10 sec, <1.5 inch)
1.5% Melamine Cyanurate intercalated & modified Clay + 10% melamine cyanurate	40.1	1580	4600	Pass (< 2 sec, <1.0 inch)
1.5% Melamine Cyanurate intercalated & modified clay + 15% melamine cyanurate	39.2	1550	4100	Pass (< 5 sec, < 1.0 inch)
1.5% Melamine intercalated & modified clay + 10% melamine cyanurate	40.4	1590	4700	Pass (<10 sec, <2 inch)
1.5% Melamine intercalated & modified clay + 15% melamine cyanurate	39.3	1628	4000	Pass (<10 sec, <1.5 inch)

Standard Deviation –Modulus<5%, Strength<5%,, Impact <12%

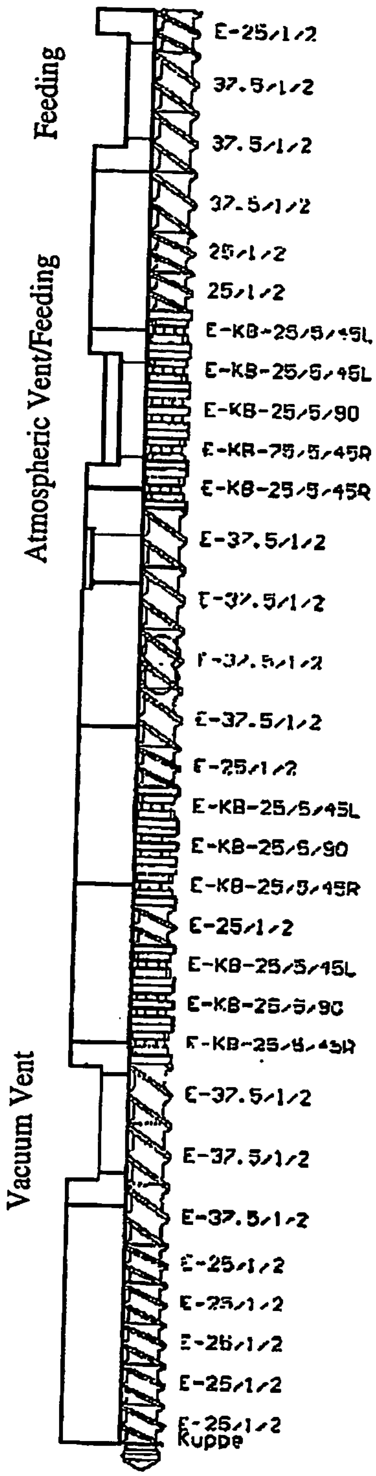
Example 15:

Cone Calorimeter Heat Release Rates(Figure 5); FAA 12 s Vertical Burn Extinguishment times (Figure 6), Tensile Strength (Figure 7); Notched Impact Strength (Figure 8)

The following example illustrates that the combination of melamine cyanurate, magnesium hydroxide, melamine modified and intercalated montmorillonite in Nylon 12 provides simultaneous improvement in heat release values, vertical burn, and tensile strength with comparable notched impact performance, compared with nylon 12 modified with melamine

cyanurate and melamine modified montmorillonite. Fire and impact performance results are superior to a commercial classically flame retarded Nylon 12 (FR N12).

It will be appreciated by persons skilled in the art that numerous variations and/or modifications may be made to the invention as shown in the specific embodiments without departing from the spirit or scope of the invention as broadly described. The present embodiments are, therefore, to be considered in all respects as illustrative and not restrictive.



Feeding
Atmospheric Vent/Feeding
Vacuum Vent
E-25/1/2
37.5/1/2
37.5/1/2
37.5/1/2
25/1/2
25/1/2
E-KB-25/5/45L
E-KB-25/5/45L
E-KB-25/5/90
E-KB-25/5/45R
E-KB-25/5/45R
E-37.5/1/2
E-37.5/1/2
E-37.5/1/2
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E-KB-25/5/45L
E-KB-25/5/90
E-KB-25/5/45R
E-25/1/2
E-KB-25/5/45L
E-KB-25/5/90
E-KB-25/5/45R
E-37.5/1/2
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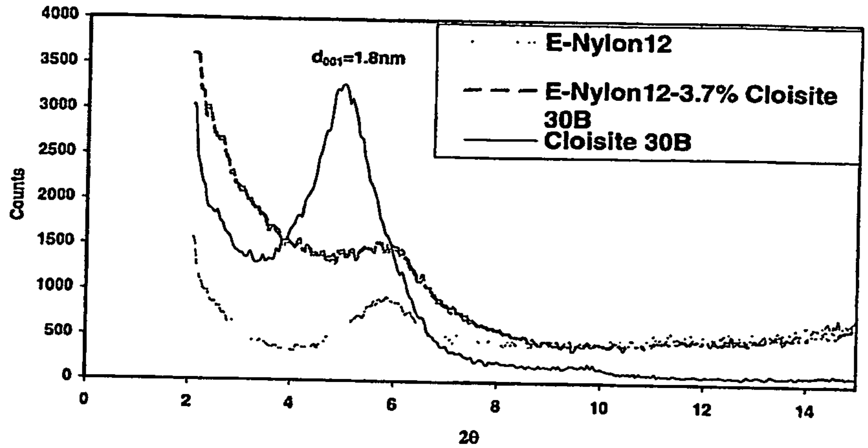
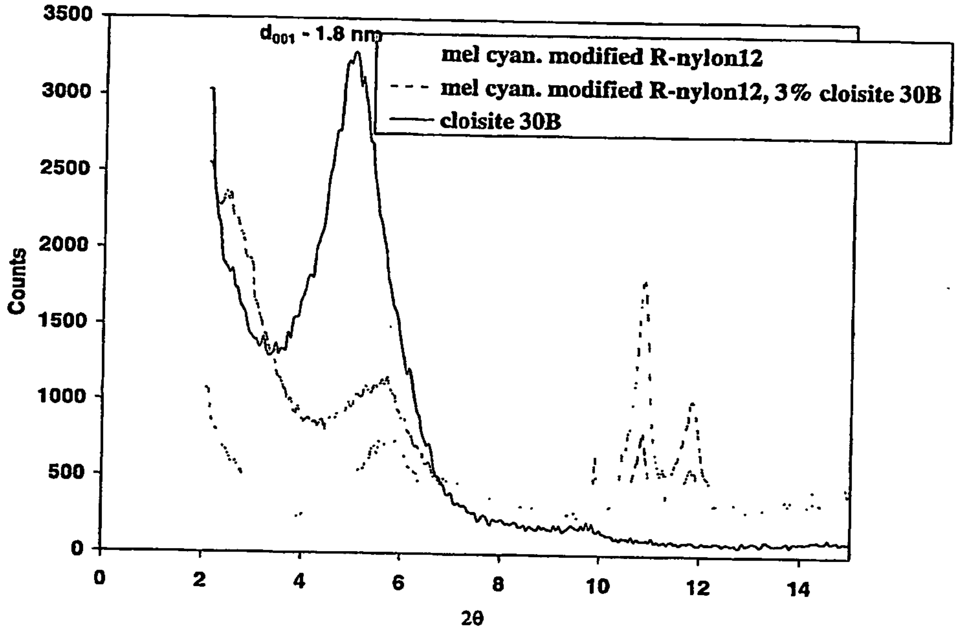
Kuppe

Figure 1



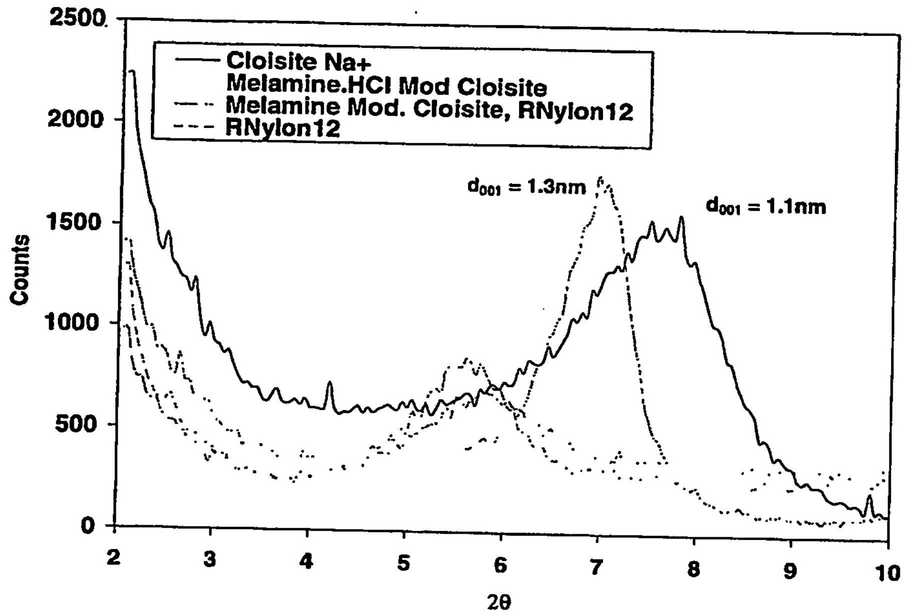
4000
3500
3000
2500
2000
1500
1000
500
0
Counts
0
2
4
6
8
10
12
14
2θ
d001=1.8nm
E-Nylon12
E-Nylon12-3.7% Cloisite 30B
Cloisite 30B

Figure 2



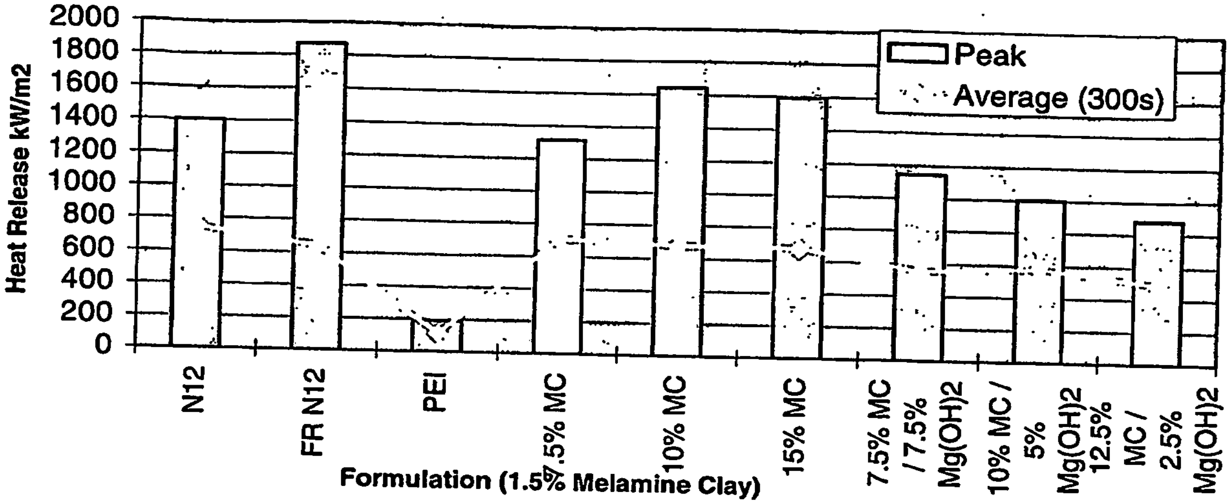
3500
3000
2500
2000
1500
1000
500
0
Counts
0
2
4
6
8
10
12
14
2θ
d_{001} - 1.8 nm
mel cyan. modified R-nylon12
mel cyan. modified R-nylon12, 3% cloisite 30B
cloisite 30B

Figure 3



Cloisite Na+
Melamine.HCl Mod Cloisite
Melamine Mod. Cloisite, RNylon12
RNylon12
d001 = 1.3nm
d001 = 1.1nm
Counts
2θ
2500
2000
1500
1000
500
0
2
3
4
5
6
7
8
9
10

Figure 4



2000
1800
1600
1400
1200
1000
800
600
400
200
0
Heat Release kW/m2
Peak
Average (300s)
N12
FR N12
PEI
7.5% MC
10% MC
15% MC
7.5% MC / 7.5% Mg(OH)2
10% MC / 5% Mg(OH)2
12.5% MC / 2.5% Mg(OH)2
Formulation (1.5% Melamine Clay)

Figure 5

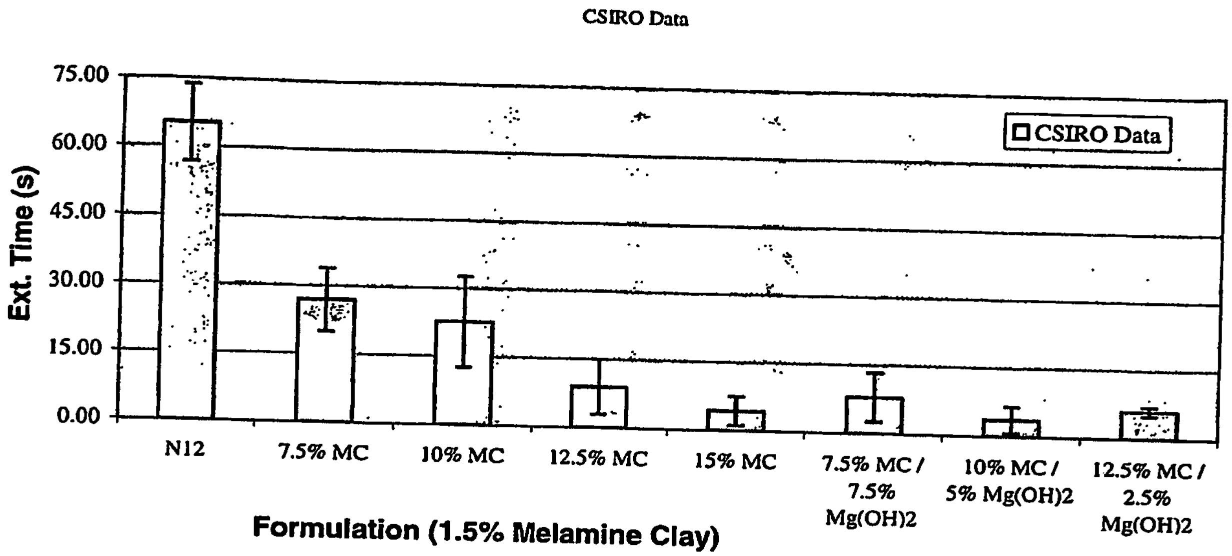

CSIRO Data
75.00
60.00
45.00
30.00
15.00
0.00
Ext. Time (s)
CSIRO Data
N12
7.5% MC
10% MC
12.5% MC
15% MC
7.5% MC / 7.5% Mg(OH)2
10% MC / 5% Mg(OH)2
12.5% MC / 2.5% Mg(OH)2
Formulation (1.5% Melamine Clay)

Figure 6

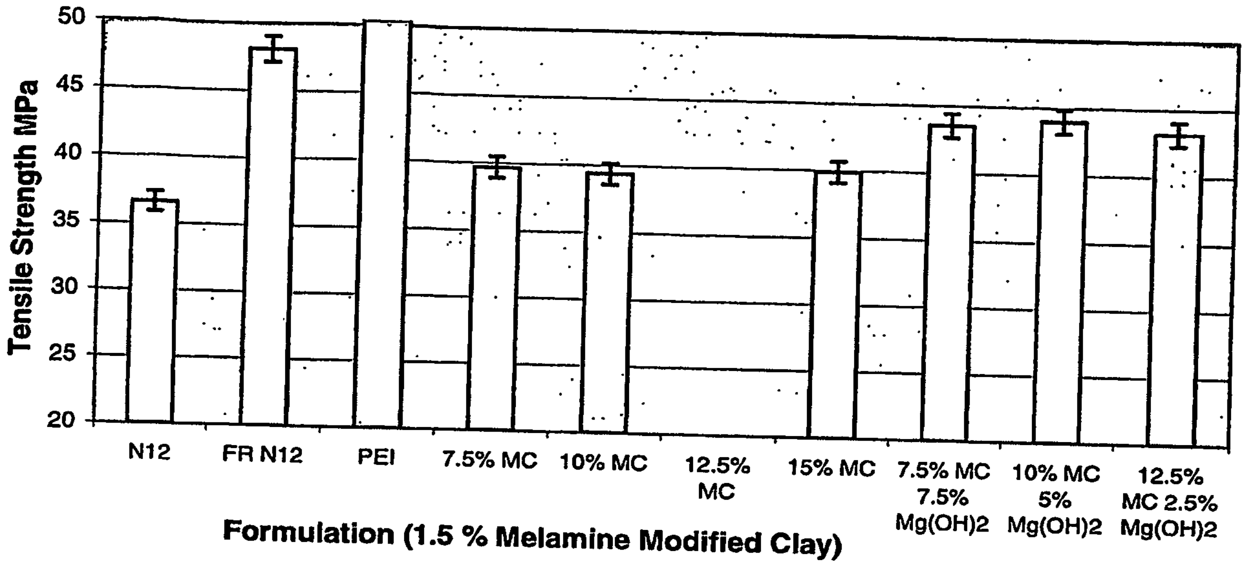

Tensile Strength MPa
50
45
40
35
30
25
20
N12
FR N12
PEI
7.5% MC
10% MC
12.5% MC
15% MC
7.5% MC 7.5% Mg(OH)2
10% MC 5% Mg(OH)2
12.5% MC 2.5% Mg(OH)2
Formulation (1.5 % Melamine Modified Clay)

Figure 7

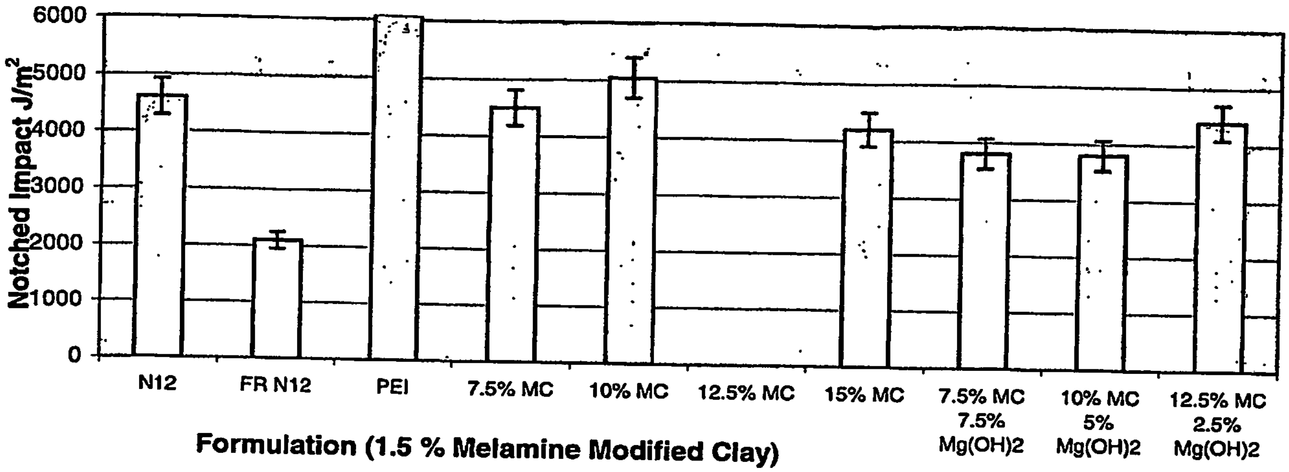

6000
5000
4000
3000
2000
1000
0
Notched Impact J/m2
N12
FR N12
PEI
7.5% MC
10% MC
12.5% MC
15% MC
7.5% MC 7.5% Mg(OH)2
10% MC 5% Mg(OH)2
12.5% MC 2.5% Mg(OH)2
Formulation (1.5 % Melamine Modified Clay)

Figure 8